

Total Selenium and Selenium (IV) in the James River Estuary and Southern Chesapeake Bay

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The concentrations of total selenium (Se) and Se (IV) were determined in the surface waters of 30 stations located in the James River and southern Chesapeake Bay. The concentrations of total Se and Se (IV) ranged from 0.28 to 1.91 nM and from 0.07 to 1.36 nM, respectively, between salinities of 31.78 and 0.06‰. The concentration of Se (VI), calculated as the difference between the concentrations of total Se and Se (IV), ranged from 0.08 to 0.67 nM. While total Se seemed to be conservative in this study area at salinities above 0.36‰, Se (IV) might have been removed during estuarine mixing. The removal of Se (IV) occurred primarily at salinities below 4‰ possibly via the oxidation of Se (IV) to Se (VI).

Introduction

Riverine input has long been recognized as one of the most important terms in the global geochemical cycle (Boyle *et al.*, 1974; Edmond *et al.*, 1981). Chemical and biological processes which occur during the mixing of river water with seawater may lead to the addition or removal, as well as the alteration, of the speciation of dissolved constituents in river waters (Liss, 1976; Aston, 1978), and thus may determine to a significant extent the riverine supply of elements to the oceans. Elements which can exist in different oxidation states are of particular interest because the true redox potential of natural waters is not precisely known (Breck, 1974) and species in the different oxidation states may behave differently during estuarine mixing (Aston, 1978). Selenium (Se) is one such element. The common oxidation states of selenium are -2, 0, +4 and +6. Sillen (1961) suggested that Se (VI) should be the only detectable species of selenium in oxygenated seawater, since the Se (IV) to Se (VI) ratio at equilibrium should be $10^{-11.5}$, and both Se (-II) and Se (0) should also be undetectable. However, the existence of both Se (IV) and Se (VI) have been reported. The concentration of Se (IV) in seawater ranges from undetectable to 0.7 nM, while the concentration of total Se in seawater ranges from 0.3 to 2.5 nM (Sugimura *et al.*, 1976; Cutter, 1978; Measures & Burton, 1980; Measures *et al.*, 1980; Uchida *et al.*,

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1980). The concentrations of total Se and Se (IV) in estuarine waters range from 0.2 to 4.5 nM and from undetectable to 0.3 nM, respectively (Kharkar *et al.*, 1968, Measures & Burton, 1978; Uchida *et al.*, 1980).

Kharkar *et al.* (1968) studied the interactions between dissolved selenium and particulate phases in the laboratory. They reported that at a selenium concentration similar to that in river water, more than 80% of dissolved selenium could be removed by adsorption onto ferric oxide and manganese dioxide in distilled water. The selenium that was adsorbed onto montmorillonite, kaolinite, manganese dioxide and peat could be desorbed when the solid phases were exposed to seawater. If these processes occur in an estuary, a production of selenium may be observed during estuarine mixing. However, Measures and Burton (1978) reported that both total Se and Se (IV) in the River Test were conservative at salinities between 7 and 34‰. In this paper, we shall discuss the speciation of selenium in the James River and southern Chesapeake Bay.

Materials and methods

Study area

Chesapeake Bay is one of the largest estuaries in the United States. It extends in a north-south direction for about 290 km (Newcombe *et al.*, 1939) and its drainage basin is about 166 200 km² (Pelczar, 1972). It has a number of tributaries. The James River is the third largest river which drains into Chesapeake Bay and it contributes 16% of the annual fresh-water input (Pritchard, 1952). It is classified as a coastal plain estuary. The tidal portion of the James River extends for 168 km from its mouth at Hampton Roads to Richmond, Virginia. The volume of water in the tidal portion of the James is approximately 2.36×10^9 m³ (Cronin & Pritchard, 1975), and an average discharge measured at Richmond is approximately 240 m³ s⁻¹ (U.S. Geological Survey, 1973). A rough estimate of the residence time of water excluding tidal flushing would be 114 days. The James River has a number of tributaries. The Chickahominy, Warwick, Nansemond and Elizabeth Rivers are the major ones within the study area. However, they have comparatively low discharge rates (Feuillet & Fleischer, 1980). Thirty sampling stations were occupied in the James River, southern Chesapeake Bay and Atlantic Ocean off Cape Henry (Figure 1). Station 1 is approximately 50 km downstream from Richmond.

Sampling and analytical methods

Samples were collected during two cruises: on 8 December 1981 for stns 1 through 23, and on 4 February 1982 for stns 24 through 30. At each station, surface water was collected with a polyethylene bucket and immediately filtered through Gelman A/E glass-fibre filters. The samples were stored in polyethylene bottles, kept in ice, and returned to the laboratory on the same day. In the laboratory, they were stored at about 4 °C and analysed within a week after the collection (Cheam & Agemian, 1980). The samples were analysed for total Se and Se (IV) as described elsewhere (Takayanagi & Wong, 1983). Briefly, total Se was preconcentrated by coprecipitation with tellurium. Se (IV) was preconcentrated by complexing it with ammonium 1-pyrrolidinedithiocarbamate, extracting the complex into chloroform and back-extracting the selenium into nitric acid. The preconcentrated selenium was determined fluorometrically. In this analytical scheme, any chloroform-extractable organic selenium will also be included as Se (IV), while Se (-II) and Se (0) may be included as total Se although the contributions from these species are expected

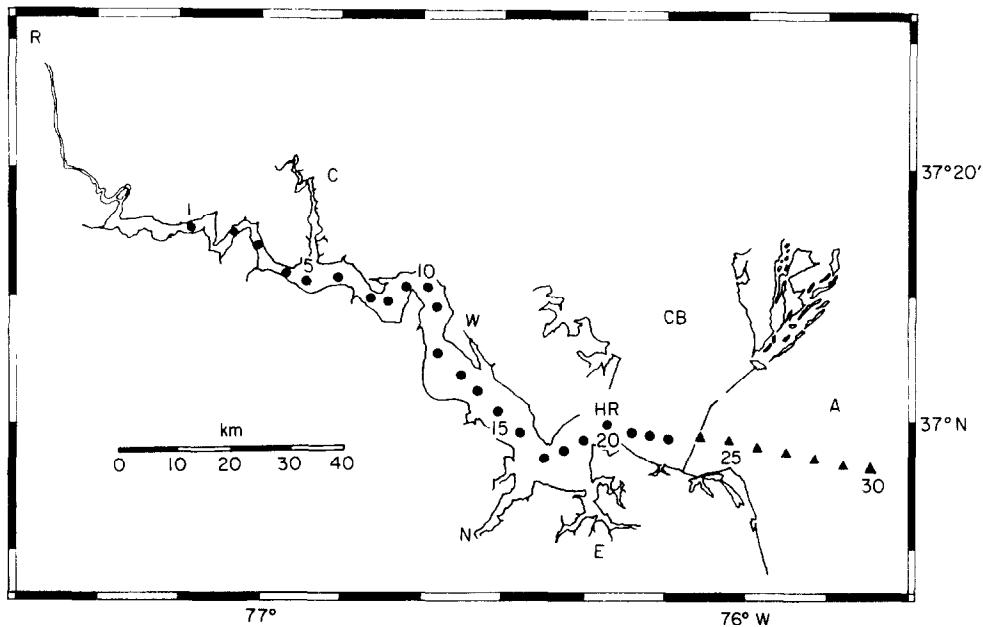


Figure 1. Sampling stations in December (●) and February (▲). A: Atlantic Ocean; C: Chickahominy River; CB: Chesapeake Bay; E: Elizabeth River; HR: Hampton Roads; N: Nansemond River; R: Richmond; W: Warwick River.

to be small (Cutter, 1982; Takayanagi, 1982). The salinities were determined with a Guildline Instruments Model 8400 salinometer.

Results and discussion

The concentration of total Se decreased with increasing salinity, ranging from 1.91 nM at 0.06‰ to 0.28 nM at 31.78‰ (Figure 2). The concentrations at high salinities are similar to those observed in the surface waters of the Atlantic Ocean (Measures & Burton, 1980). Total Se correlates linearly with salinity with a correlation coefficient of 0.98 between 31.78 and 0.36‰, implying that total Se is conservative within this range of salinities. The concentration of total Se at 0.06‰ (1.91 nM), lies significantly above this theoretical dilution line. Since only one data point is involved, the interpretation is somewhat tentative. This sample has been analysed repeatedly and the same result was obtained. We have no reason to suspect that the composition had been modified during sampling or storage. There are two possible reasons for this anomaly. Total Se may have been removed in the waters at salinities below 0.36‰. Iron and humic substances have been reported to be removed by flocculation at low salinities (<1‰) (Sholkovitz *et al.*, 1978; Sholkovitz & Copland, 1981). Since some of the dissolved selenium may exist in the colloidal form in natural waters (Sigleo & Helz, 1981; Takayanagi & Wong, 1982), flocculation induced by salinity changes may remove selenium as well. Alternatively, the elevated concentration at 0.06‰ may be caused by the natural variability of the concentration of total Se in the riverine endmember. Anomalously high concentrations of dissolved organic carbon and ammonia have also been observed at this station (unpublished results).

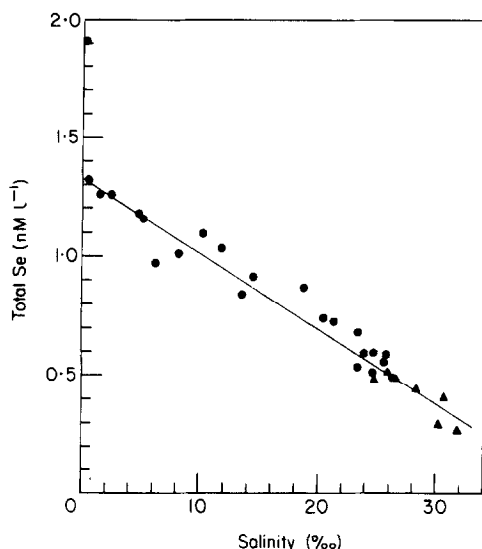


Figure 2. Total Se against salinity in the waters collected in December (●) and February (▲). Uncertainty of an individual point is ± 0.02 nM. The linear regression line for the data points with salinities above 0.06‰ is also shown.

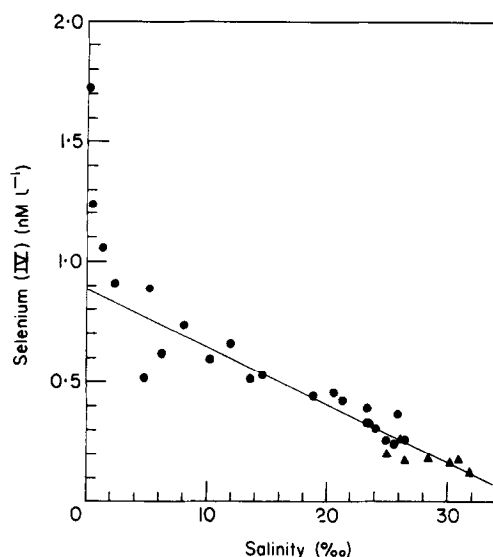


Figure 3. Se (IV) against salinity in the waters collected in December (●) and February (▲). Uncertainty of an individual point is ± 0.02 nM. The linear regression line for the data points with salinities above 4‰ is also shown.

The concentration of Se (IV) also decreased with increasing salinity with a range of 1.72–0.12 nM (Figure 3). The concentration of Se (IV) correlates linearly with salinity at salinities above 4‰ with a correlation coefficient of 0.93. Below this salinity, all the data points lie above this dilution line. This suggests that Se (IV) is non-conservative during estuarine mixing and may be removed primarily in the waters at salinities below 4‰. Since only one sample at the riverine endmember was analysed and temporal variations in the concentration of Se (IV) might have occurred, the removal of Se (IV) cannot be

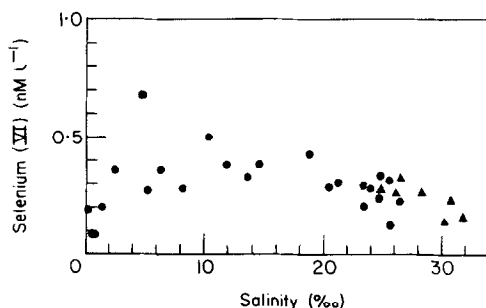


Figure 4. Se (VI) against salinity in the waters collected in December (●) and February (▲). Uncertainty of an individual point is ± 0.04 nM.

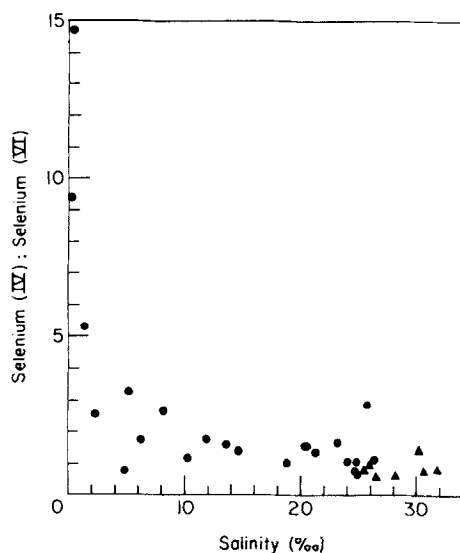


Figure 5. The concentration ratio of Se (IV) to Se (VI) against salinity in the waters collected in December (●) and February (▲).

quantified accurately. However, if the concentration of Se (IV) of 1.72 nM at a salinity of 0.06‰ does represent the composition of the riverine endmember, the amount of Se (IV) removed in this estuary may be estimated by the method of Boyle *et al.* (1974). Since the intercept of the dilution line is 0.88 nM, 0.84 nM of Se (IV), or about 50% of the riverine input, has been removed in the waters at salinities less than 4‰ . There are several possible mechanisms for the removal of Se (IV) during estuarine mixing: conversion to a particulate form by processes such as biological uptake and adsorption onto suspended particles; or conversion to another dissolved form via processes such as the oxidation to Se (VI). Although the specific biochemical role of selenium is not well understood, it is recognized as an essential trace element for the healthy growth of organisms (Frost & Lish, 1975; Thomson & Robinson, 1980; Mertz, 1981). Accumulation of selenium by zooplankton and marine invertebrates have been reported (Fowler & Benayoun, 1976*a, b*; Wrench, 1978). Wrench (1978) reported that marine phytoplankton, *Tetraselmis tetrathele* and *Dunaliella minuta*, were capable of taking up Se (IV) in culture media. He also suggested that selenium was assimilated as seleno-analogues of the sulphur amino acids. Sandholm *et al.* (1973) however, reported that the uptake of Se (IV) by green algae, *Scenedesmus*

dimorphus, was negligible in 60 min. If Se (IV) is actively consumed by organisms, biological uptake may be one of the possible removal mechanisms during estuarine mixing. Since Se (IV) is known to be easily adsorbed onto ferric hydroxide (Geering *et al.*, 1968), a major carrier phase in estuaries, adsorption onto suspended particles is also a plausible removal mechanism. However, since total dissolved Se is approximately conservative between 31.78 and 0.36‰, the conversion of Se (IV) to a particulate form is unlikely, at least within this range of salinities.

The concentration of Se (VI) may be estimated as the difference between the concentrations of total Se and Se (IV). Since total Se is conservative while Se (IV) is removed in the waters at salinities above 0.36‰, this model will indicate that Se (VI) is produced during estuarine mixing by the oxidation of Se (IV) to Se (VI). Indeed, most data points lie above the theoretical dilution line connecting the riverine and oceanic endmembers (Figure 4). Rosenfeld & Beath (1964) reported that the rate of transformation between Se (IV) and Se (VI) is slow in pure inorganic systems. However, in the natural water system, organisms may be able to increase the rates of oxidative reactions significantly. Morris *et al.* (1978) suggested that in the low salinity regions of the Tamar Estuary, oxygen utilizing bacteria could be responsible for the oxidation of organic matter and other reduced species such as Fe (II) and Mn (II). Emerson *et al.* (1982) also observed the bacterial-catalysed oxidation of Mn (II) in the waters of Saanich Inlet.

Se (IV) is the predominant species of selenium in river waters. With increasing salinity, the concentration ratio of Se (IV) to Se (VI) decreases from 15 at 0.36‰ to around 0.9 at 31.78‰ (Figure 5). The decrease was most dramatic at salinities below 10‰. At salinities above 10‰, the ratio was rather constant. However, even at the oceanic endmember, the ratio is still much higher than the value predicted by thermodynamic equilibrium, and it is only slightly higher than the values reported for open ocean seawaters, which range from 0 to 0.7 (Measures & Burton, 1980; Measures *et al.*, 1980).

Conclusions

Se (IV), a thermodynamically unstable species, was the dominant dissolved inorganic species of selenium in the James River. Total Se was conservative at salinities above 0.36‰. However, a significant amount of Se (IV) was removed during estuarine mixing at salinities below 4‰ possibly as a result of the oxidation of Se (IV) to Se (VI).

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